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Flavonoids Syntheses. Ⅵ. Synthesis and Spectral Properties of 4-Arylcoumarins (Neoflavones).

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Eight neoflavones (5, 7-dihydroxy-, 5, 7, 2′-trihydroxy-, 5, 7, 3′-trihydroxy-, 5, 7, 4′-trihydroxy-, 5, 7, 2′, 5′-tetrahydroxy-, 5, 7-dihydroxy-2′-methoxy-, 7-hydroxy-, and 7, 3′-dihydroxyneoflavone) were prepared by the Pechmann condensation of phloroglucinol or resorcinol with benzoylacetic acid ethyl esters for examination of their spectral properties. In the mass spectra, the neoflavones lacking an O-function at C-2′ showed stable fragments of 〔M^+-28〕 caused by decarboxylation. On the other hand, in the case of 2′-oxygenated neoflavones, dehydroxylation or demethylation between C_5-OH and substituents at C-2′ occurred to give 〔M^+-17〕 or 〔M^+-59〕. Other spectral data showed no specific features that could be used to characterize the structures.

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Novel Flavonoids from the Fern *Notholaena sulphurea*.

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The major constituent of the yellow frond exudate of the fern *Notholaena sulphurea* was identified by spectroscopic methods as 3, 5, 2′-trihydroxy-7-methoxy-8-acetoxyflavone and its structure was confirmed by synthesis. This novel natural flavonoid was also detected in the frond exudate of five other *Notholaena* species. In the yellow form of *N. sulphurea*, the rare 5, 2′-dihydroxy-7,8-dimethoxyflavone was also found, along with some trivial flavonoids. The white form of *N. sulphurea* produces three dihydrochalcones that are accompanies by some kaempferol methyl ethers and apigenin-7-methyl ether. The 3-acetoxy as well as the 3-butyroxy and the 4′-butyroxy derivatives of 7-methyl aromadendrin were also identified in this material.

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Synthesis of Flavonoids in *Scutellaria* spp. Ⅱ. Synthesis of 2′,6′-Dioxygenated Flavones.

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Five flavones dioxygenated at C-2′ and C-6′ (5, 7, 2′, 6′-tetrahydroxy- (**1**), 5, 7, 2′-trihydroxy-6′-methoxy- (**2**), 5, 2′-dihydroxy-7,8,6′-trimethoxy- (**3**), 5,2′, 6′-trihydroxy-7,8-dimethoxy- (**4**) and 5,7,2′-trihydroxy-8, 6′-dimethoxyflavone (**5**)) have been isolated from *Scutellaris* spp.. Among them **1** and **2** were isolated from *S. baicalensis*, **3** was from *S. rivularis*, **4** was from both *S. baicalensis* and *S. viscidula*, and **5** was from *S. discolor*, respectively. To confirm these constituents characterized the genus *Scutellaria*, syntheses of **1**–**5** were described in this paper. Spectroscopic comparison of the synthetics with the corresponding natural flavones confirmed the respective structures.